# Modification of Si nanoparticle structure through co-condensation in plasma flash evaporation of Si-Al binary powder feedstock

A. Tanaka<sup>1</sup>, M. Kaga<sup>1</sup>, R. Ohta<sup>1</sup>, M. Dougakiuchi<sup>2</sup> and M. Kambara<sup>1</sup>

<sup>1</sup>Department of Materials Engineering, The University of Tokyo, Tokyo, Japan <sup>2</sup> Shimane Institute for Industrial Technology, Shimane, Japan

**Abstract:** Si nanoparticles have been produced by plasma flash evaporation using Si and Al powder feedstock. Two different injection methods were employed to modify the Si structure through different heating and cooling histories in the plasma flame. The structures and formation path of these Si nanoparticles as well as the battery properties were compared.

Keywords: Si, nanoparticles, nanorod, plasma spray, condensation, lithium-ion battery.

## 1. Introduction

Lithium-ion batteries are expected to be used as large capacity storage in electric vehicles so that high density electrode such as Si needs to be adopted as it possesses 10 times greater gravimetric and volumetric capacities than the conventional graphite. This material however experiences large volume change during battery reactions, causing cracks and pulverization thereby reducing the capacity in short battery cycles. Feasible solution for this issue is structuring the active materials at nano-to-micro meter length scale, such as nanoparticles [1], pore structure [2], nanowire [3,4] and coating with electric and electrochemically stable elements [5]. As the potential secondary element, Al is promising as it is electrical conducting and electrochemically active not to produce irreversible capacities [6], as long as it is structured at nanometer length scale despite dilation with lithiation, similar to Si. Another interesting feature of Al addition is that Al can act as a catalyst for Si nanowire growth if its molten state coexists with Si vapor [7,8].

There are many reports on production of these composite active materials. From the processing point of view, however, many of processes require multiple lengthy structuring steps and are not necessarily compatible with the current industry process in terms of production throughputs [9]. In this respect, plasma flash evaporation (PFE) can be a selection as it is an industry process that utilizes low-cost feedstock for nanoparticle production at high throughputs. In fact, improved high capacities are attained after 100 cycles using metallurgical grade Si at a rate of 1 kg/h [10]. Furthermore, from Si and Cu powder mixture, composite Si nanoparticles on which Cu nanoparticle is directly attached are produced through cocondensation and the battery cycle stability is improved. Quite recently, continuous Si nanorod growth is also confirmed using Cu as catalyst by the controlled injection in PFE. In this work, therefore, to seek for the possibility of further modification of Si nanostructure, two ways of co-condensation with Si and Al mixture were investigated.

### 2. Experimental

The Si nanoparticles were produced by plasma flash evaporation (PFE) using metallurgical grade Si powder (mean diameter: 15  $\mu$ m, purity: 99.9%) and Al (20  $\mu$ m,

99.9%) as raw material. Thermal plasma was generated with DC and RF hybrid plasma torch system under the typical condition at which complete evaporation of Si was confirmed [10]. Plasma jet was immediately quenched in the water-cooled vessel that is placed under the plasma torch so that nanoparticles through condensation were collected at the wall of the vessel after plasma was turned off. Raw powders were injected into plasma by two ways: (i) mixed-injection (*m*PFE) where Si and Al mixture powders are injection at the same time from the center of the plasma torch, (ii) separate-injection (*s*PFE) where Si is injected from top of the torch whereas Cu is injected from the bottom of the vessel to the lower temperature zone of the plasma jet. The typical process conditions are listed in Table 1.

The collected nanoparticles were characterized by XRD, SEM, TEM. Also after being sieved with 40  $\mu$ m mesh, the nanoparticles were mixed with electric conducting carbon and polyimide binder to form slurry and the anode is prepared by following the standard casting procedure. 2016 half coin cells were then assembled with Li foil as counter electrode and 1M LiPF<sub>6</sub> with EC:DEC=1:1 (vol:vol) electrolyte in a globe box. At least 5 cells were prepared for each nanoparticle. The battery cycle test was conducted at constant current mode with 0.02C for the first 3 cycles and 0.1C for the remaining cycles.

Table 1. Typical conditions used in PFE.

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Parameter	Value
DC power (kW)	9
RF power (kW)	90
Radial Ar flow rate (slm)	140
Tangential Ar flow rate (slm)	30
Radial $H_2$ flow rate (slm)	50
Al addition (at.%)	0 - 30
Si powder feeding rate (g/min)	1.0
Deposition time (min)	10
Chamber pressure (Torr)	400
Ar upflow for sPFE (slm)	50

# 3. Results and discussion

3.1. Si nanoparticles by mPFE

Figure 1 shows the XRD patterns of the particles produced by *m*PFE with different Al contents. It is seen that all processed particles include crystalline Si regardless

of the amount of Al, and the Al crystalline peaks become stronger as the Al initial content increases. The average Si crystallite size evaluated by the Rietveld analysis of these XRD patterns are in the 20 - 40 nm range, indicating that the fundamental nucleation and growth of Si is not affected significantly by the addition of Al.



Fig. 1. XRD patterns of the Si-NP by mPFE.



Fig. 2. STEM-ADF image and EELS intensity distributions across the Si-NP by mPFE.

The STEM image and EELS line intensity of the Si-NP with 10 at%Al are shown in Fig. 2. Al with 10 nm is observed to attach directly onto the Si-NP with 40 nm, similar to the case of Cu addition [11]. The total enthalpy necessary for a complete evaporation of Al is 280 kJ/mol at 2623 K, which contrasts to 303 kJ/mol at 2843 K for Cu and 386 kJ/mol at 3507 K for Si. Considering also the same feedstock particle size, it is plausible that the feedstock Si and Al powder mixtures are evaporated completely and nanoparticles are produced via co-condensation of Si-Al vapor mixtures.

Based on the classical nucleation theory, the nucleation point is estimated as shown in Fig. 3 and is indicated by the intersection of the threshold supersaturation for nucleation and the experimentally-determined supersaturation. Si is expected to nucleate at 2200 K irrespective of the Al content while Al will nucleate at 1400 K for 10 at% and at 1300 K for 1 at% addition. In contrast, the heterogeneous nucleation point of Al onto a Si substrate is 1650 K for 10 at% and 1500 K for 1 at%Al. Although the nucleation barrier for the secondary element in general increases with reducing the Si particle size by the factor given by the shape factor (Fig. 4), the value of factor for 20 - 40 nm particle is somewhat similar to that for a flat substrate. Therefore, for any Al addition condition, Si is supposed to nucleate first during cooling at 2200 K and grow as molten nanoparticle, then later at 1600 - 1500 K, Al potentially

nucleates directly on a Si nanoparticle. This nucleation sequence reasonably explains the formation of the composite Si:Al-NP observed in Fig. 2. At high Al content, although many smaller Al nuclei will attach onto Si particle, they may tend to coarsen due to low melting point.

Another important finding of the EELS analysis is that oxygen is detected especially at the same position with Al, indicating that Al is more preferentially oxidized than Si. Since no oxygen is introduced in the plasma, oxidation must have occurred during collection from the vessel.



Fig. 3. Temperature dependence of supersaturation for (a) Si and (b) Al homogeneous nucleation under the present PFE condition. The heterogeneous nucleation of Al onto Si substrate (c). Solid line: nucleation threshold, dotted line: experimental.



Fig. 4. Particle size dependence of the shape factor for heterogeneous nucleation of several elements. Unity of shape factor stands for the case of homogeneous nucleation and  $f(\theta)$  for the case on a flat substrate.

Figure 5 shows the capacity and coulombic efficiency of the cells using the *m*PFE nanoparticles. It also compares with those of the cell using *m*PFE Si only and of the cell with a simple mixture of PFE Si and PFE Al. Slow oxidation in chamber under 100 Pa for 12 hours was applied upon powder collection of PFE Al. As a general tendency, relatively high capacities are maintained at least 10 cycles but they fade with cycles afterwards. The first cycle efficiency for the cells with Al doped particles reaches 75% on average which is comparable with the

value 74% for the cell with Si only. However, the capacity seems to decay rather faster if Al is doped. In particular for 1% Al addition, the capacity decreases rapidly after 10 cycles, while the capacity becomes comparable with that of the Si only anode when the Al content increases to 30 at%. Further increase in Al to 50 at%, however, the capacity decreases again. As is seen from the EELS compositional analysis shown in Fig. 2, Al is preferentially oxidized, which should become more significant for smaller Al particles due to the increased specific surface area. In this sense, since the size of the Al nanoparticles attached on Si-NP for 1 at% should be smallest among the specimens, the electrical conduction path within the anode would be lost easily, resulting in the rapid fade of the capacity. The reduced capacity for 50 at% will be simply due to the reduced ideal capacity because of Al inclusion.

If one compares with the capacity of the cell using the mixture of PFE Si and PFE Al, the coulombic efficiency is improved especially at the initial stage of the cycles and higher capacities are maintained after 100 cycles. It is therefore suggested that Al addition is fundamentally effective to improve the battery cyclability, but to use the most of this effect, one needs to operate PFE and the subsequent process at controlled environment not to allow oxidation of the materials.



Fig. 5. Variation of capacity (a) and coulombic efficiency (b) for the half cells using the mPFE particles as anode.

#### 3.2. Feasibility of structural modification by sPFE

When Si and Al raw powders are injected together from the top of the plasma torch, both are immediately evaporated to form Si and Al vapor mixture, so that the structure of the materials, such as Si nanoparticle growth and the subsequent Al attachment, is controlled fundamentally by the sequence of the nucleation events. This in turn indicates that as long as both elements are injected together to form high temperature vapor, Si inevitably condenses first and the secondary element will follow and attach on the Si particle because Si should be the primary element to be an active material for battery. Therefore, to utilize Al as the effective catalyst for Si nanowire growth, according to the VLS growth, molten Al should co-exist with Si vapor during condensation. This is only possible by introducing Al separately to the lower temperature position of the plasma flame so that Al will melt to form droplet while Si evaporates to form vapor. Indeed, for the case of a separate injection of Si and Cu powder feedstock, in which Cu is introduced from the bottom of the vessel to the lower temperature region of the plasma flame, Si nanorods are observed to form with the Cu cap, and its overall growth process including the formation of Cu droplet catalyst and Si growth from the Cu as a catalyst can be reasonably explained based on the VLS and directional growth. This is quite unique in that Si nanorod can be produced continuously by a single process at greater throughputs using the powder feedstocks only, which is clearly distinguished from the conventional approach. In the present work, such a separate injection PFE is employed for the Si and Al powder feedstock and compared with the case of Si and Cu binary system.

Prior to the sPFE experiment, Al particle heating history along the Ar upflow gas streamline from the vessel bottom is simulated. The plasma gas temperature and velocity distributions are calculated with Comsol commercial software and typical streamlines from down- and up-flow that meet each other are selected as shown in Fig. 6. Along this streamline, the Al particle heating history is calculated following the conventional approach [12]. As a representing particle, 5 µm diameter Al particle is found to evaporate completely before it arrives at the collection point. At the other end of the particle size, the particle with 140 µm diameter is expected not to melt completely under the present condition. If the particle size is 20 µm, it can be completely melted and even partly evaporated before it arrives at the collection point. On the other hand, as discussed in the previous section, Si is expected to nucleate at 2200 K and its timing corresponds approximately to 3 ms after Al particle injection at which 20 µm Al becomes already at the molten state. That is, molten Al can coexist with Si vapor, indicating that the requirement is satisfied for the catalyzed nanowire growth by the VLS mode.



Fig. 6. Al particle heating history in the vessel. Dotted lines are the typical streamline of up- and down-flow. Solid lines show the temperature history of the Al particle that flows on a upward gas.

The size of the molten Al particle can be reduced during flight as a result of partial evaporation and the size at the collection point is the size of catalyst, which determines the Si nanorod diameter. At the position (4) where Si nanorod was observed for the Si-Cu injection, for example, the Al particle size distribution was calculated as shown in Fig.7(a), exhibiting that the molten droplet size at the collection point (red) is not so much different from that of the raw powders (black) under the present condition. In addition, to work as a catalyst, Al droplet needs to capture enough Si during flight so that Si is saturated for growth. The total amount of Si vapor/Si clusters that impinge to the Al droplet during flight is calculated based on Hertz-Knudsen and its size dependence is shown in Fig. 7(b). Due to the different specific surface, Si concentration increases as droplet size decreases, and the droplet with 10 µm attains the Si concentration at the eutectic point of Si-Al system. Considering all phenomena, Al particles with size ranging from 5 to 10 µm can actually become a catalyst to grow Si when Al droplet is cooled at the collection point of the vessel. Even larger particles can also act as catalyst if enough amount of Si vapor/nanocluster is supplied after attaching at the vessel wall.



Fig. 7. (a) Comparison of the Al particle size distribution between in the raw powders and at the collection point, and (b) calculated Si content in the Al droplet.

Figure 8 shows the XRD patterns of the Si-Al materials that are processed by sPFE and collected at the different positions in the vessel. Roughly the temperature decreases from the position 1 (directly exposed to the plasma) to 5 (at the exit of the vessel). Irrespective of the different collection position, i.e. different temperature history, there is no noticeable difference in the present phases, except the slight decrease in the Al amount at closer to the exit.

SEM and EDS mapping images of the materials collected at the position (4) are shown in Fig. 8. It is difficult to find Si nanorod similar to the ones observed for the Si-Cu case.



Fig. 8. XRD patterns for the sPFE materials collected at different positions in the vessel.



Fig. 9. SEM and EDS image (b & e) Si and (c & f) Al for the sPFE Si materials at the position 4.

Rather spherical Al particles with around 1  $\mu$ m are scattered and small distorted Si seems to grow from this Al. Majority of Al however is seen to be much larger and its shape is not quite spherical. In fact, if molten Al droplet as large as 10  $\mu$ m impinges onto the vessel wall, it tends to deform to form splat quite similarly to a droplet in plasma spray coating. If this is the case, the flattened droplet surface becomes wide so that the length of Si could be inevitably short because of mass conservation and Al may solidify quickly due to increased heat extraction, both of which could hinder a directional growth of Si with certain length accordingly.

# 4. Conclusion

Si nanoparticle structure can be fundamentally modified by controlling the co-condensation path of the Si-Al binary system. However, in order to configure the structure applicable to LiB anode, oxidation needs to be effectively suppressed. Also, to form Si nanorod by sPFE in the Si-Al system, due to a smaller enthalpy for complete evaporation for Al than Cu, relatively larger particles become the molten catalyst at a fixed heating gas stream. To produce genuine nanosized Si rod, smaller Al feedstocks are to be injected to much lower temperature zone (but high enough to melt Al completely).

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